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(54) Deposition process.

(57) A deposition process especially suitable for coating
plastics substrates with transition metals such as chro-
mium comprises vapour depositing the metal on to the
substrate and bombarding the deposit with energetic
particles. The bombardment reduces tension and/or
causes compression in the deposit thereby producing a
better quality finish.

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DESCRIPTION

1 This invention relates to deposition processes.

Vacuum deposition is a well known process, and various modifications of the process are described in the following documents:-

5 U.S. Patent No. 3,523,387 discloses an apparatus for substrate modification including cleaning that employs evaporant and ion sources. U.S. Patents Nos. 3,904,505 and 3,961,103 disclose apparatus and process that, in one embodiment, employ together evaporant and ion sources for deposition. The article "Physics of
10 Ion Plating and Ion Beam Deposition" by Aisenberg (inventor of U.S. '505 and '103 above) et al, J. Vac. Sci., Vol. 10, No. 1, Jan. 1 Feb., 1973 pp. 104-107 discloses concurrent use of evaporant and ion sources for deposition.

The article "The Compressive Stress Transition in Al, V,
15 Zr, Nb and W Metal Films Sputtered at Low Working Pressures," by Hoffman (an inventor herein) and Thornton in THIN SOLID FILMS 45 (1977) 387-396 discloses stress alteration through sputtering at low pressures using magnetron plasma confinement and also discloses that bias sputtering can alter deposit stress.

20 The article "Stress in Ion-Implanted CVD Si₃N₄ Films" by EarNisse in JOURNAL OF APPLIED PHYSICS, Vol. 48, No. 8, August 1977 discloses stress alteration in CVD deposits of Si₃N₄ insulators on silicon using ion bombardment.

Although Vapour deposition and ion bombardment processes
25 have been disclosed before, hitherto no-one has appreciated that these techniques can be used to improve the internal stress, and other properties, e.g. optical reflectance, of metaldeposits.

According to the present invention, there is provided a deposition process, which comprises depositing a metal on to a
30 substrate from the vapour phase, and bombarding the deposit with energetic particles, characterised in that the energy and number of energetic particles are sufficient to alter the internal stress of the deposit.

1 The bombardment of material deposited by vacuum deposition, e.g. b, metallization from evaporant sources, enhances the deposition process. An advantageously low ratio of energetic particles to other deposition particles yield, when the energetic particles
5 are sufficiently accelerated, deposits that have desirable internal stress. As few as 1 or 2 energetic particles per 200 deposited particles may bring about desired change (e.g. diminish tensile stress, bring about compressive stress) and even smaller ratios can be employed, if desired.

10 In depositing a transition metal such as chromium vapour that normally deposits in tension, bombardment of its deposits by energetic particles of, for example, inert gas can modify the metal deposit to have compressive stresses comparable in magnitude to tensile stresses that occur without bombardment.

15 This stress modification is preventative of cracking and peeling of the deposit from the substrate. Furthermore, with metal as chromium, bombardment that causes stress change in the deposit also can improve reflectance.

20 The energetic particles are preferably in the form of ions and may, for example be of inert gas or a metal. Preferably the ions are of the same element as that used for the deposition.

25 Since only a few energetic particles per otherwise deposited particle yield desirable modification, substrates such as heat resistant plastics may be used without their deformation, degradation and the like, even when relatively thick films, e.g., over 1000⁰A are deposited.

30 Preferably, an evaporant source is used in conjunction with a stress modifying level of energetic particles that is below that which causes undesirable substrate heating so that high quality thin metal films can be deposited rapidly on heat sensitive materials. Plastics materials may therefore be used as the substrate.

35 The bombardment may be carried out during the deposition, or after the deposition.

35 A diverse group of materials are depositable from vapour

1 in a vacuum and can be employed in accordance with this invention.
As these materials or derivatives thereof constitute that which
will comprise most, by weight, if not all, of the deposit on the
substrate, they will for convenience, be called herein "primary
5 deposition materials".

The primary deposition materials for which this invention
is especially applicable are metals which normally form deposits
that are in tension from vacuum operations such as by vapour
deposition from evaporant sources. Refractory transition metals
10 constitutes one such class of metals and suitable metal may be
selected therefrom, particularly for example, for improved optical
reflectance when deposition is otherwise with less than desired
reflectance from evaporant sources. Thus, suitable metals may
include any selected from the following as well as alloys (e.g.
15 stainless steel) based on (or containing) one or more of the
following: titanium, vanadium, chromium, iron, nickel, cobalt,
molybdenum, platinum, palladium, rare earth as gadolinium, ruthen-
ium, zirconium, rhodium, niobium, osmium, rhenium and other such
metals that are of Groups IIIa-VIIa and VIII of the Periodic
20 Table. Some non-refractory materials may also be used, e.g.
aluminum 6061 alloy may also receive desired stress alteration when
deposited from vapour.

Of transition metals, the first series transition metals
such as chromium illustrate a particular value of this invention.
25 Chromium, and its bright alloys, for example, normally deposit from
evaporant sources in an undesirable off-colour and in tension that
restrict use from evaporant sources. Other deposits besides those
of the first series as chromium that similarly may derive benefit
from this invention include niobium, molybdenum, tantalum and
30 gadolinium and alloys based on any of such metals.

In a first embodiment, this invention comprises utilizing
deposition from an evaporant source of primary deposition material,
e.g., resistively, electron bombarded or otherwise heated source,
in a vacuum chamber desirably maintained at levels below about
35 10^{-2} Torr, especially below about 10^{-4} Torr, and as is illustrated

- 1 in Figure 1. Although any source or sources of vapour or vapours
 of the primary deposition material including charged species there-
 of may be used, evaporant sources offer special advantage as to,
 for example, convenience, power efficiency and rapid deposition.
- 5 The precise vacuum pressure during such deposition is not normally
 a critical feature of this invention. As is understood with any
 deposition process, however, partial pressure of interfering or
 deleterious substances (e.g., partial pressure of reactive oxygen
 during deposition of chromium) should be kept as low as possible.
- 10 When vapours are inert or desirably included, they may be within
 the vacuum at varying vapour pressures differing from the above
 recited average pressures of the vacuum chamber (e.g. vapour pres-
 sure of primary deposition material at its source or at its deposi-
 tion destination).
- 15 In this first embodiment, using an evaporant source, a
 substrate is placed in the vacuum so as to permit contact with the
 vapour and formation of a deposit on the substrate with the primary
 deposition material. The substrate may be of conducting or non-
 conducting material. This invention offers advantage in that heat
20 sensitive substrates as plastics, e.g., those commonly known as
 "ABS", may be employed when depositing thin films. Advantageously,
 the substrate may be prepared for deposition by bombardment with
 energetic particles prior to any vapour deposition. Such prior
 bombardment can cause a sputtering off of surface contaminants and
25 can provide a more adhering substrate surface.

The order in which the energetic particles bombard the
vapour deposit is not critical. Rather, the flux of depositing
vapour as well as the flux of energetic particles may be varied as
desired. For example, the energetic particles may continuously or
30 intermittantly bombard the deposit as it is being built-up. More-
over, the energetic particles may bombard the deposit during a time
when it is not being built-up or not being built-up as rapidly as
during another time.

In one advantageous manner of still further mitigating
35 substrate heating, if desired, the substrate or sources may be

1 moved relative to one another thereby varying the amount of vapour
and energetic particles contacting the substrate with time. Thus,
for example, substrate that is to receive deposition of primary
deposition material may be rotated, translated or otherwise moved
5 between locations of high vapour flux and high energetic particle
flux so as to disassociate, at least in part, heating effects due
to each and permit intermediate cooling, if desired. For thick
films, such sequential vapour deposition and energetic particle
bombardment may advantageously use more than two sources of, or
10 rotation or oscillation between, sources of vapour and energetic
particles. Such sequence may be repeated many times, e.g. 100
or more.

One convenient approach is to use, as energetic particles,
particles as ions from separately actuated ion sources, as ion guns
15 which are conventionally known and commercially available. The ion
guns can be external to the chamber wherein vapour deposition occurs
and actuated as desired. Ions of inert gas, e.g., krypton, argon,
xenon, or primary deposition material, e.g., chromium or even neu-
tral particles or beams, e.g., mixed ions and electrons, or other
20 atoms as nitrogen, may be employed.

At any given energy level in this or other embodiments, a
certain amount of experimentation may be required to determine the
relative number of energetic particles per particles of primary
deposition material for any particular substrate employed in order
25 that the deposit advantageously have desired stress and other
physical properties. The final chosen number of energetic particles
at any given energy for industrial processes may also depend on
secondary factors such as power consumption, deposition and bombard-
ment rate, nature of primary deposition material, bombarding spe-
30 cies, substrate material including its capacity to withstand heat,
film thickness required and the like. Unless the minimum number
for each energy level of bombarding particles per otherwise depos-
iting particles is reached, however, for desired stress change, no
significant effect is seen. As before, this minimum number is
35 advantageously low.

1 It is important, however, that not too high a number of
energetic particles at a given energy level be used that would lead
to undesired sputtering of the deposited primary deposition material
after its deposition. Such sputtering can cause erosion of the
5 deposit surface as well as possible other degradation of film
character.

Thus, for example, in concurrent bombardment and vapour
deposition processes, upon establishment of the dose of energetic
10 particles at a given energy level that alters stress from tension
to compression and provides desirable reflectance, the number of
energetic particles should desirably not exceed say be a factor of
20, preferably, a factor of 10 or less, the number of energetic
particles that is critical to achieve change from tension to
compression.

15 While experimentation may, as above suggested, be useful
for optimal levels of energetic particles, a range of up to about
30 or even less, e.g., about 0.1-5, energetic particles as inert
gas ions and the like at about 0.1-30 Kev, per 100 deposited parti-
cles of primary deposition material as chromium and its bright
20 alloys, when using an evaporant source of such primary deposition
material and separately activated ion gun, is normally sufficient
on non-conducting substrates. Higher ratios of energetic particles
per otherwise depositing particles may be advantageous if the
energetic particles are ions or atoms of the same type as the
25 primary deposition material, especially when at the lower of the
recited energies. Moreover, higher energy energetic particles
(e.g., 300 Kev) may be used necessitating only lower ratios of
energetic particles for desired effect, providing, of course, undue
sputtering by the highly energetic particles is not encountered and
30 the deposits are sufficiently thick.

The measurement of internal stresses of deposits can be
accomplished by any convenient method as, for example, those
reported by D. S. Campbell in "Handbook of Thin Film Technology"
Maissel and Glang, eds. p. 21-1, McGraw-Hill. For metals as chro-
35 mium, a simple comparison (with the eye) is normally adequate to

- 1 distinguish between (a) deposition as from an evaporant source and
(b) deposition modified by energetic particles. This is because
chromium and its bright alloys show correlation between reflective
brightness and deposition in compression.
- 5 A particular advantage of the method of this invention is
that no external biasing of the substrate need be made. Rather, the
source of energetic particles may be separately actuated at desired
levels and directed or otherwise allowed to contact the substrate
with deposits of primary deposition material thereon. This separate
10 actuation allows for use of several sources of energetic particles
of varying types concurrently or sequentially, if desired, and
precise control of film quality, especially on curved substrates.
- 15 It is not altogether clear from present evidence whether
or not it is the kinetic energy or momentum of the energetic
particles that is fundamentally related to stress modification of
deposited films. Knowledge of the precise relationship is not,
however, necessary for practice of the invention as the ending
stress characteristics can be readily controlled by controlling
the amount of energetic particles at any given energy level.
- 20 An advantageous aspect of this invention is that thick
films, e.g., above about 1000 \AA thick, as for instance, 2000 \AA -
20,000 \AA or more of chromium or its alloys or other decorative metals
on heat resistant or cooled plastic substrate may be deposited.
Such thick films can be accomplished, for example, as follows.
- 25 Chromium or bright alloy is evaporated into a chamber
maintained at pressures in a range below about one millitorr
whereupon deposition begins on the plastic substrate in the vacuum.
A source of energetic particles, e.g., ions of inert gas, atoms or
ions of chromium and the like are introduced into the vacuum to
30 contact chromium deposit as it is being deposited from the evapor-
ant source. The energetic particles required to produce compres-
sive stress increases are desirably at about 0.5-15 Kev or more and
the number of energetic particles at these energy levels lies betwe-
en about 0.2-20 per 100 evaporant atoms of chromium or bright alloy
35 that are in the deposit. The bombarding of the deposits of vapour

- 1 by the energetic particles is continued until the ending deposit is a thick film as above described and has its stress characteristics showing deposition stress about zero or slightly or even greater in compression as desired for a particular application.
- 5 Alternatively, the contacting with the energetic particles may be intermittent (e.g. after a 1-4000 \AA thick film has been vapour deposited) with similar results.

During the period of deposition no external bias, as previously mentioned, need be applied to the substrate, although, 10 such external bias may, if desired, be applied.

The following examples are provided to illustrate certain aspects of this invention as previously described and is not intended as limiting the scope of this invention. In the examples, reference is made to the accompanying drawings, in which:-

- 15 Figure 1 illustrates schematically an apparatus adapted for use in this invention with separate ion source and evaporative source.

Figure 2 illustrates graphically results of Example 1 by showing stress change along with reflectance change for chromium 20 deposits that are bombarded with varying numbers and energy levels of energetic particles.

Figure 3 illustrates graphically results of Example 2 and shows effect of substrate temperature on stress of deposited film.

- 25 Figure 4 illustrates schematically another apparatus for use in this invention with separate ion and evaporative sources.

EXAMPLE 1

Figure 1 illustrates in schematic fashion an arrangement of apparatus that may be used to deposit films in accordance with this invention.

- 30 In this apparatus, a Colutron ion source 2 is used to produce energetic particles such as ions. The gas to be ionized enters the chamber of the source 2 through a needle valve 4 which adjusts flow so that the gas pressure within the chamber 2 is in the 5 to 100 millitorr range. The pressure within the rest of the

1 vacuum system is kept below 2×10^{-4} torr to prevent undesirable
loss of ion beam current and to prevent incorporation of impurity
gas atoms within the films being grown.

An arc is established between a resistively heated filament 6 (partially surrounded by ceramic insulator 9) and an anode 8 of the ion source, providing a dense plasma in the vicinity of the filament and anode. Ions are extracted from this plasma through an aperture 10 in the ion source and accelerated to a desired energy, (e.g. 1 to 15 Kev) by applying a positive voltage 10 on the ion source relative to the grounded extraction lens 12. The ions drift through the extraction lens and through other ion optics (not shown, but located between extraction lens 12 and aperture 20) into the chamber of the vacuum system 18. An aperture 20 is used to limit the extent of the ion beam within the chamber.

15 A resistively heated source 22 (power supply not shown) provides a controlled rate of deposition of, for example, chromium onto a pair of substrates 24a and 24b on substrate holder 26 mounted on a rotatable carousel 28 (the rotary vacuum feedthrough and mechanical linkage is not shown). By rotating the carousel the 20 ion beam may strike either or both of the substrates. An ion collector 30 may be rotated into proper orientation to monitor the ion beam current. By measuring this current, which is usually kept constant in this example, the flux of ion bombardment upon a substrate may be determined. Device 16 is a quartz crystal film 25 monitor.

The ion beam collides with one of the substrates 24a while at the same time chromium is being evaporated onto the pair of substrates. The second substrate 24b accumulates approximately the same chromium deposit as substrate 24a; however, for comparison 30 purposes substrate 24b is not bombarded with ions. A movable shutter 34 (mechanical linkage not shown) permits control of which substrate is bombarded with ions.

Figure 2 illustrates graphically the results of deposition of chromium on glass (rate of about $3\text{A}/\text{second}$) using the above 35 described apparatus in accordance with the invention. The X axis

is per cent of ions bombarding the vapour deposited metal on the substrate. The Y axis is optical reflectance for curve A and stress for curve B.

From curve A it may be seen that reflectance is beneficially altered by certain doses of 12 Kev ions of xenon. From curve B it can be seen that stress is also altered by certain dose of xenon, energetic ions at 12 Kev.

By comparing curves A and B, it can be seen that optical brightness also correlates with deposition of film in compression at the same ratios of energetic particles at the same energy level.

The film thicknesses of chromium in this Example are approximately 2000 \AA . The absolute dose in Figure 2 is uncertain and the critical dose could be 1/3 less than the 0.9 μ indicated. The dose is relative in Figure 2 and the purpose of this Figure 2 is to illustrate optical reflectivity change of the same dose at which stress becomes compressive.

EXAMPLE 2

Using the procedures of Example 1, bombardment is with argon ions rather than xenon ions. Also, the temperatures of the substrates bombarded are monitored and controlled. Temperature control (60°C) of substrates bombarded is with heat sink to a massive copper block using liquid gallium - indium eutectic. "Hot substrates" are glass allowed to warm up to combined power input to the substrates (e.g. from radiation, ion beam current, and chromium condensation). It is estimated that the "hot substrate" temperature exceeds 200°C .

Figure 4 shows results of dose (ions per 100 deposited atoms) versus internal stress of chromium films at the different temperatures. The results are shown with smooth curves which are estimated from data points that are not greater than $\pm 25\%$ from the curve. Stress is determined as noted above.

EXAMPLE 3

The ions of xenon at 12Kev of Example 1 are replaced by

- 12 -

1 ions of chromium and the procedures of Example 1 using the apparatus
of Figure 1 are repeated with similar results.

EXAMPLE 4

5 The procedures of Example 1 are again followed with
respect to ion-modified deposition using the apparatus of Figure 1
except that the vapour deposition and ion bombardment are conducted
sequentially by permitting a buildup of 200^Å layers of chromium
before beginning bombarding with the ions of inert gas. The per-
cent of ions bombarding the 200^Å layers of chromium is varied in
10 accordance with Figure 2. The results show similarly desirably
improved stress and reflectance at critical doses.

EXAMPLE 5

15 The procedures of Example 1 are followed except that
alternative evaporative source 22' is employed rather than source
22 and the movable shutter 34 is not used. Carousel 28 is filled
with several spaced substrates and is rotated to provide alternating
vapour deposition and ion bombardment for the substrates as it
rotated. Desirable stress and brightness are seen with chromium
deposition modified by argon ions at 12 Kev.

EXAMPLE 6

20 Figure 3 illustrates a coating apparatus for deposition
onto a large area at high rates on stationary or moving
(translated and/or rotating) substrates or parts. The components
shown are:

25 1. Industrial-sized diffusion pumped vacuum chamber 100
with capability for pressure maintenance at or below 10⁻³ torr;
provision for continuous or semicontinuous introduction and removal
of workpieces to be coated by means of separately pumped vestibules
102 and 104, and vacuum gate valves (not shown); fixturing (not
shown) for translation and/or rotation of workpieces 120 through
the chamber.

- 1 2. High-rate electron beam heated evaporator 106 with continuous introduction of evaporant 112 by rod feed that has evaporation capacity on the order of 0.1-10 cc of metal per minute per source.
- 5 3. Ion beam source 108 of ion-milling type (large area, high current density, neutralized beam) that provides 0.5 milliamp/cm² of ionized argon 110 over 30 centimeter diameter. (Apparatus can employ multiple evaporation and ion sources to cover enlarged areas as desired). Operating parameters are adjusted to obtain
- 10 high rate deposition with sufficient dose of accelerated ions to produce compressive-bright films accordingly as in Example 1 and as hereinbefore described. Owing to the sharp-transition nature of the phenomenon (see Fig. 2) it is not necessary that the ion dose be everywhere uniform, but only that it exceed (but desirably not
- 15 by more than a factor of 15) the minimum required dosage, as determined in specific application by examination of film quality.

CLAIMS

- 1 1. A deposition process, which comprises depositing a metal on to a substrate from the vapour phase, and bombarding the deposit with energetic particles, characterised in that the energy and number of energetic particles are sufficient to alter the internal stress of the deposit.
- 2 2. A process according to Claim 1 wherein the metal comprises a transition metal.
- 3 3. A process according to Claim 1 wherein the metal comprises chromium or an alloy thereof.
- 10 4. A process according to any one of Claims 1 to 3 wherein the bombardment is effected whilst the metal is being deposited.
- 5 5. A process according to any one of Claims 1 to 3 wherein the bombardment is effected after the deposition.
- 15 6. A process according to any one of Claims 1 to 5 wherein the substrate comprises a plastics material.
- 20 7. A process according to any one of Claims 1 to 6 wherein the energetic particles comprise ions.
- 8 8. A process according to Claim 6, wherein the ions have an energy of from 0.1 to 30 Kev.
- 25 9. A process according to Claim 7 or Claim 8 wherein the ratio of ions to atoms of vapour is in the range of from 0.1:100 to 30:100.
- 30 10. A process according to any one of Claims 7 to 9 wherein the ions are of an inert gas.

1 11. A process according to any one of Claims 7 to 9 wherein ions are of a transition metal.

12. A process according to Claim 11 wherein the ions are of chromium.

5 13. A process according to any one of Claims 1 to 12 wherein the metal is one which tends to form a deposit in tension.

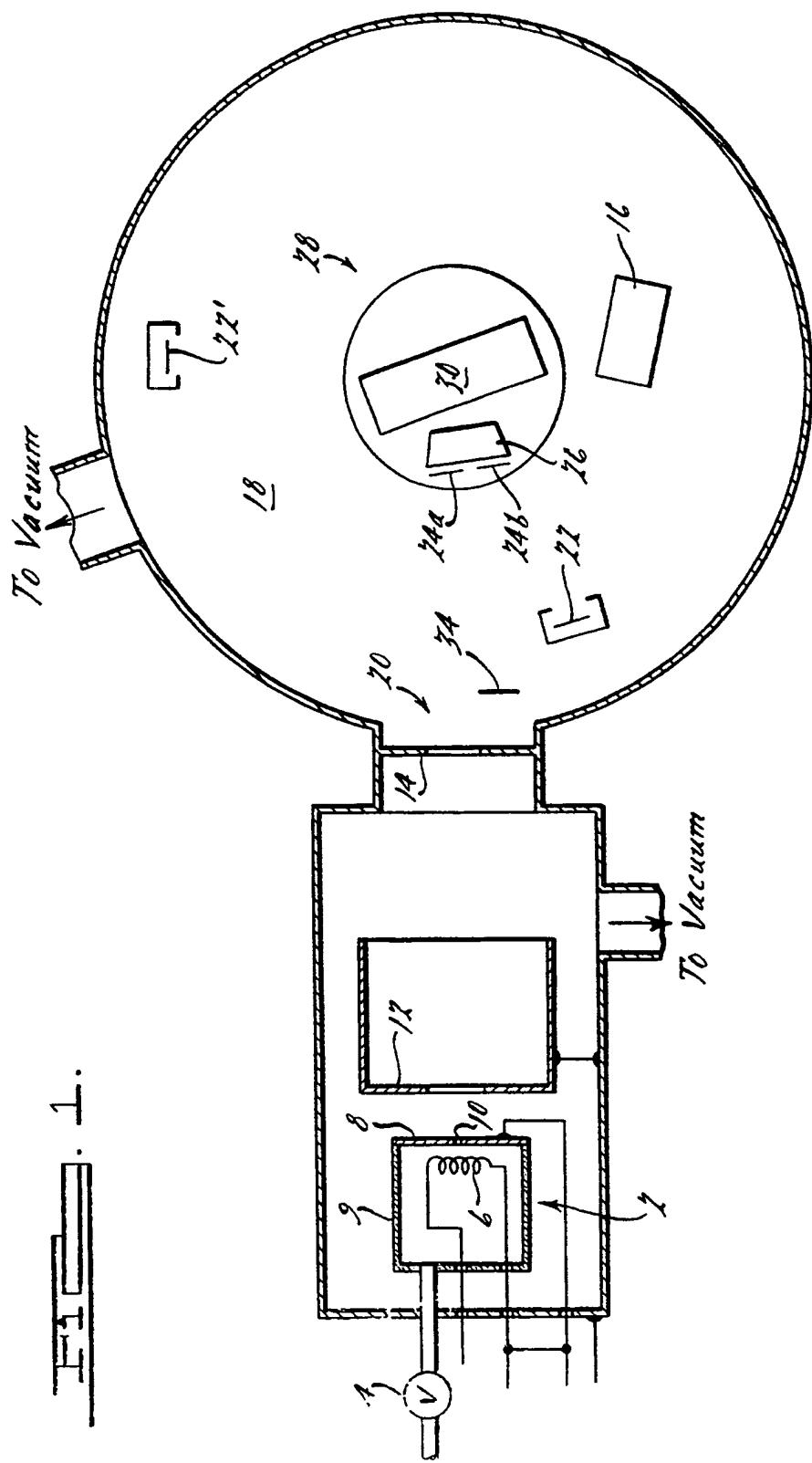
14. A process according to any one of Claims 1 to 13 wherein the deposit is in compression after bombardment.

15. A process according to any one of Claims 1 to 14
10 wherein the deposition and the bombardment are carried out by causing relative movement between the substrate and a first location containing the metal at a high vapour density, and a second location containing the energetic particles, whereby the substrate is sequentially exposed to the high vapour density and
15 the energetic particles.

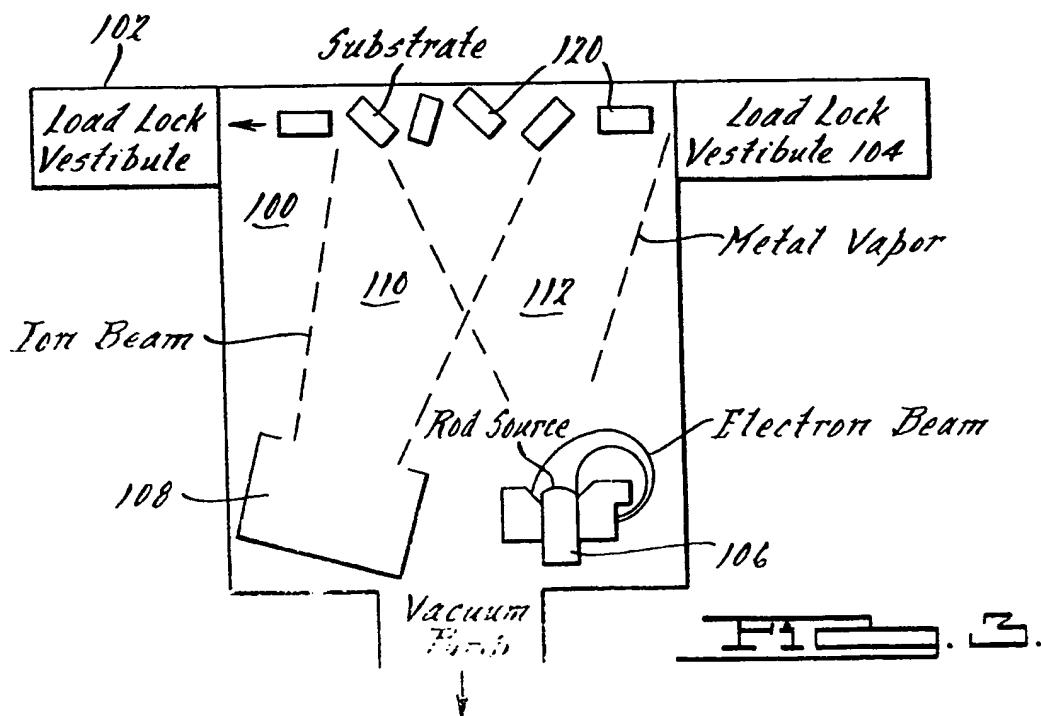
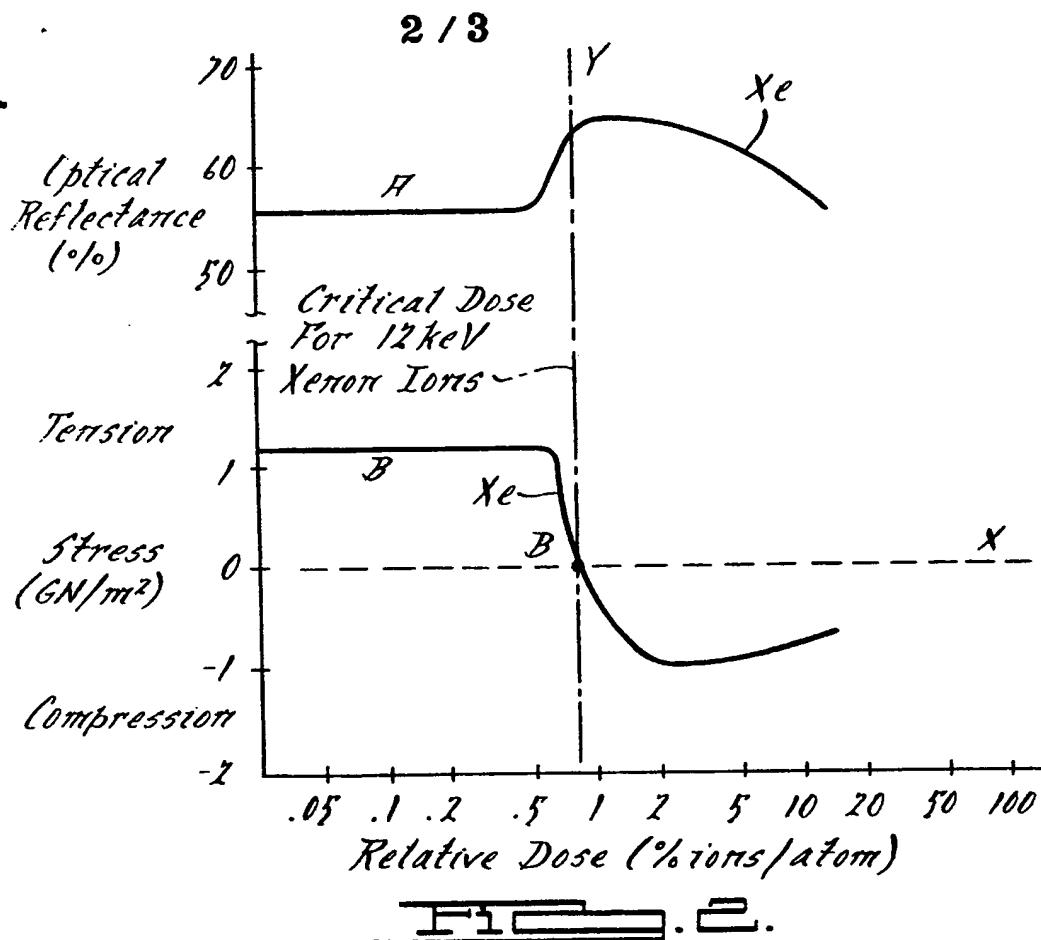
16. A process according to Claim 15 wherein the substrate is advanced through the first and second locations.

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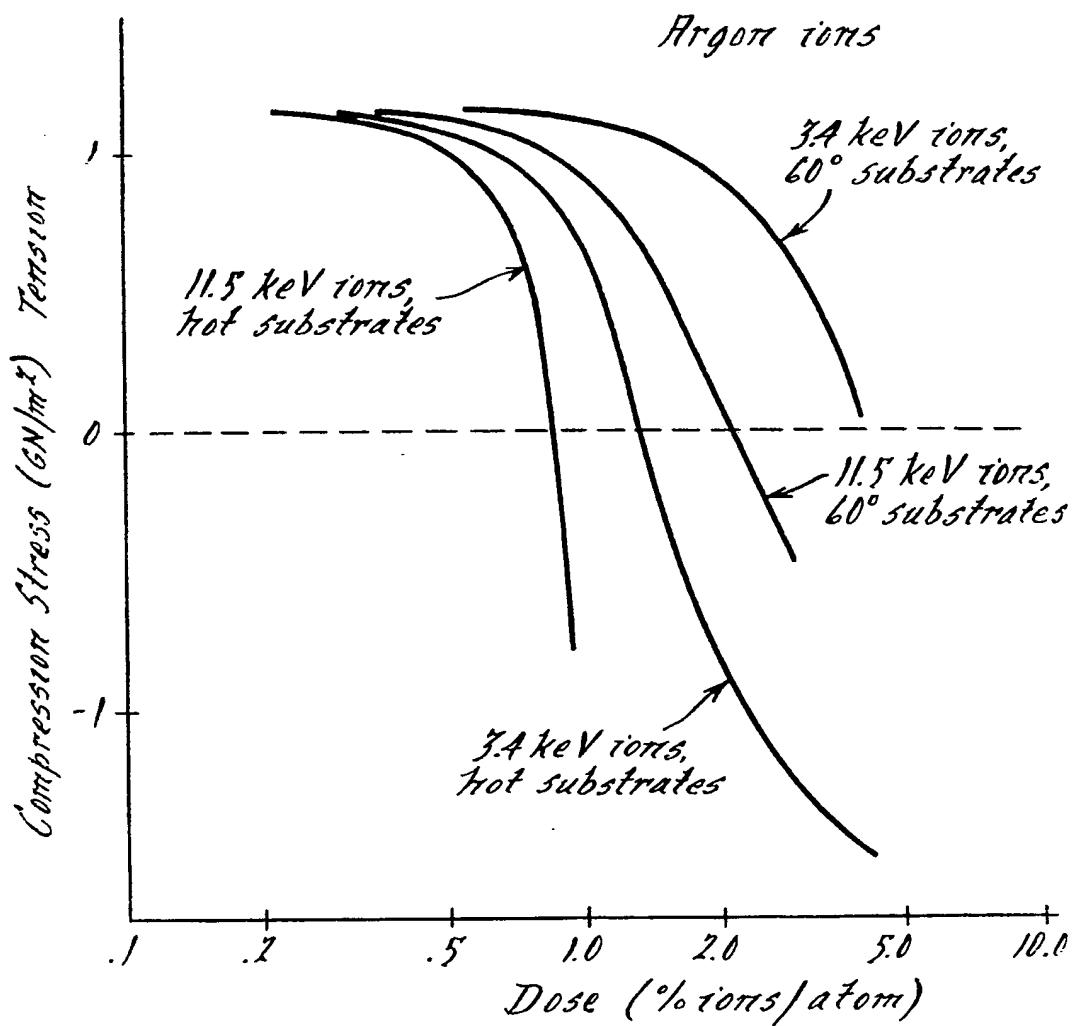


Fig. 4.

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